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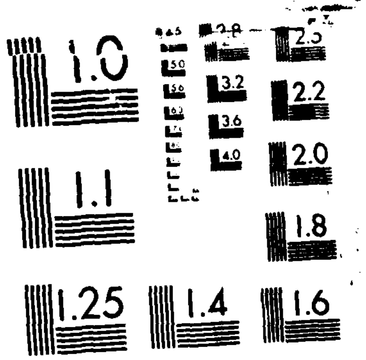

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A New Form of Ruthenium Tetracarbonyl

by

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Abstract

Irradiation of concentrated solutions of triruthenium dodecacarbonyl (III) in tetrahydrofuran and hydrocarbon solvents under one atmosphere carbon monoxide yields a purple-red compound, IV. Elemental analyses are consistent with IV having the stoichiometry $Ru(CO)_4$, while the very low volatility and solubility in organic solvents suggest that IV has a high molecular weight. Reactions of IV with carbon monoxide, hydrogen, bromine, iodine and carbon tetrachloride essentially duplicate the corresponding reactions of (III), suggesting that the two compounds are isomeric, but reactions of IV with tertiary phosphines *yield mononuclear* rather than cluster ruthenium compounds. It is therefore proposed that IV has a rather novel, possibly cyclic, structure consisting of $[Ru(CO)_4]_n$ chains.

At present there are known only three binary carbonyl compounds of ruthenium, $Ru(CO)_5$ (I), $Ru_2(CO)_9$ (II) and $Ru_3(CO)_{12}$[1] (III). Of these, III is the thermodynamically most stable, and is formed spontaneously when either of the others is allowed to stand in the absence of a partial pressure of CO. However, I can be readily prepared either thermally or photochemically from reactions of III with CO, while II can be formed by low temperature photolysis of I[1].

While extending an investigation[2] into the utilization of ruthenium carbonyls as precursors for catalysts for CO and CO_2 hydrogenation, we have had cause to prepare I photochemically from the reaction of CO with III[3]. Interestingly, we have found that photolysis of concentrated solutions of III (p_{CO}= 1 atm) in tetrahydrofuran or hydrocarbon solvents leads to formation, in addition to I, of an insoluble, purple-red material which appears to be an oligomeric form of $Ru(CO)_4$ (IV). We describe below the physical and chemical properties of IV which lead us to this conclusion[4].

Experimental

$Ru_3(CO)_{12}$ (III) was prepared from $RuCl_3 \cdot 3H_2O$ by the method of Johnson and Lewis[6], while photochemical reactions were performed using quartz apparatus and a Hanovia lamp positioned about 1 cm from the reaction mixture. Solvents were dried and degassed prior to use, and all operations were carried out under an atmosphere of carbon monoxide or nitrogen. IR spectra were run on a Bruker IFS 85 FTIR spectrometer, and gas chromatography experiments were carried out with an HP 5880A equipped with an n-octane Porasil-C column. X-ray powder diffraction patterns were obtained utilizing a CSS/Stoe STADI 2/PL two circle diffractometer. The data, along with comparable data for III, are being submitted to the JCPDS International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081. Carbon and hydrogen analyses were performed by the Canadian Microanalytical Service, Ltd, ruthenium analyses (neutron activation) by the Analytical Services Unit at Queen's, utilizing the SLOWPOKE-II facility at the Royal Military College of Canada.

Preparation of $[Ru(CO)_4]_n$ (IV). A solution of 1.00 g (1.6 mmol) III in 200 mL THF at about 20° C was photolysed for 12 hr under an atmosphere of CO. A first crop of 0.3 g (30% yield) of IV was scraped from the inner cooling jacket of the photochemical apparatus, and the decanted solution was rephotolysed to give a further 0.2 g. This procedure could be repeated to give total yields of at least 80%. The product was washed by prolonged suspension in THF to remove residual III, and was dried <u>in vacuo.</u> It is a microcrystalline solid, non-volatile and highly insoluble in the common organic solvents. Anal. Calcd for C_4O_4Ru: C, 22.54; H, 0; Ru, 47.4. Found: C, 22.04; H, <0.1; Ru, 46.9. The IR spectrum in the regions 400-700 and 1900-2150 cm^{-1} (KBr disc) is shown in Fig. 1, where it is compared with an IR spectrum of $Ru_3(CO)_{12}$ run under similar conditions.

In contrast to the above, photolysis of <u>dilute</u> solutions of III (less than 0.05 g in 200 ml solvent) results in the formation only of I.

Reaction of IV with CO. A suspension of 0.1 g of IV in petroleum ether (bp 40-60°) in a glass-lined 300 mL Parr Stirring Minireactor was treated with about 50 atm CO at 80° C for 16 hr. After cooling and opening of the reactor under nitrogen, the solution was found to contain (IR) only I (ν(CO)= 2037(s), 2002(vs) cm^{-1}) and III (ν(CO)= 2061(vs), 2032(s), 2012(m) cm^{-1}).

Reaction of IV with H_2. Similar reaction with hydrogen resulted in the formation only of $H_4Ru_4(CO)_{12}$, identified initially by comparison of its IR spectrum (ν(CO)= 2081(s), 2067(vs), 2030(m), 2024(s), 2008(w) cm^{-1}) with that of an authentic sample[7]. A $CDCl_3$ solution of the compound exhibited a hydride resonance at δ-17.8 ppm, in agreement with the literature[7].

Reactions of IV with Halogens. A mixture of 0.025 g (0.12 mmol Ru) of IV and 0.03 g (0.12 mmol) iodine in 15 ml methylene chloride was stirred for 48 hr at room temperature under nitrogen. The suspension of IV gradually disappeared, the solution turning yellow. An IR spectrum of the solution showed the presence of cis-$Ru(CO)_4I_2$ (ν(CO)= 2195(w), 2105(vs), 2095(s), 2067(s) cm^{-1}), identified by comparison with the spectrum of an authentic sample[8], and weak peaks indicating the presence of a small amount of $Ru_3(CO)_{12}I_6$ (ν(CO)= 2124(m), 2065 (partially obscured), 2014(s) cm^{-1})[8]. Similar reaction with even an excess of bromine at 0° C yielded only cis-$Ru(CO)_4Br_2$ (ν(CO)= 2175(m), 2133(s), 2104(s), 2071(s) cm^{-1})[8], although $Ru_3(CO)_{12}Br_6$[8,9] (ν(CO)= 2133(m), 2065(s, br), 2009(w)) and $Ru_2(CO)_6Br_4$ (ν(CO)= 2132(s), 2068(vs), 2004(m) cm^{-1}) were also formed as secondary products at higher temperatures.

Reaction of IV with Carbon Tetrachloride. A suspension of 0.2 g of IV in 10 mL CCl_4 was refluxed under nitrogen for 96 hr, after which time all of the starting material had gone into solution. An IR study showed that the solution contained $Ru_2(CO)_6Cl_4$[8-10] (ν(CO)= 2140(m), 2082(s), 2076(vs), 2027(m), 2018(m) cm^{-1}), but no chloroform could be detected by gc. Similar treatment of III yielded the same compound.

Reaction of IV with Tertiary Phosphines. A suspension of 0.07 g (0.33 mmol Ru) of IV in 30 mL petroleum ether (bp 40-60°) containing 0.046 g (0.33 mmol) PMe_2Ph was refluxed under nitrogen for 3 hr. The resulting blood-red solution was shown (IR) to contain a mixture of $Ru(CO)_4(PMe_2Ph)$ (major, primary product, ν(CO)= 2062(m), 1979(m), 1949(s) cm^{-1})[11] and $Ru(CO)_3(PMe_2Ph)_2$ (ν(CO)= 1897 cm^{-1})[11]. Similar products were formed with PMe_3, but no reaction occurred with PPh_3 even after refluxing for 6 days.

Discussion

As described in the Experimental Section, although photolysis of dilute solutions of $Ru_3(CO)_{12}$ (III) under one atmosphere of CO results in the expected[3] formation of $Ru(CO)_5$ (I), similar treatment of concentrated solutions results in the preferential formation of a hitherto unidentified ruthenium carbonyl compound (IV). Elemental analyses are consistent with the formulation $[Ru(CO)_4]_n$, and the possible presence of a hydride ligand seems excluded by the observation that reaction of IV with refluxing carbon tetrachloride does not yield chloroform[12].

The chemistry of IV duplicates that of III in many key ways. Thus IV reacts with carbon monoxide to form a mixture of I and III; III reacts similarly to form I reversibly[1]. Compound IV also reacts with hydrogen to form $H_4Ru_4(CO)_{12}$. We have confirmed a report[7] that III does likewise, finding that the IR and NMR spectra of the compounds obtained from the two reactions are identical.

Reactions of **IV** with halogenating reagents also duplicate those of **III**. Iodine and bromine both react below room temperature to form the compounds cis-$Ru(CO)_4X_2$ (X= Br, I), as reported for **III** and confirmed by us, although the halide-bridged species $Ru_2(CO)_6X_4$ and $Ru_3(CO)_{12}X_6$ can also be formed as secondary products at higher temperatures. Similarly, the compound $Ru_2(CO)_6Cl_4$ is obtained on refluxing **IV** in carbon tetrachloride. It has been reported that **III** yields $Ru_2(CO)_6Cl_4$ on heating in chloroform[13], and we obtain the same product on refluxing **III** in carbon tetrachloride.

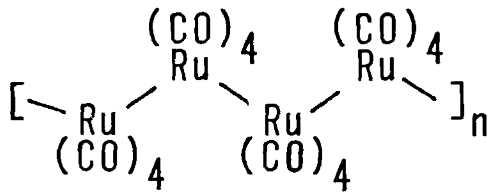
Compound **IV** was also found to react with PMe_2Ph and PMe_3 (but not with PPh_3) to form compounds of the types $Ru(CO)_4L$ and $Ru(CO)_3L_2$ (L= PMe_2Ph, PMe_3). The tetracarbonyl species appear to be the primary products, and these are known to react rapidly with tertiary phosphines under the reaction conditions used to form the corresponding tricarbonyl compounds[14]. Reactions of **III** with all three tertiary phosphines occur under similar conditions, yielding cluster compounds of the type $Ru_3(CO)_9L_3$[15].

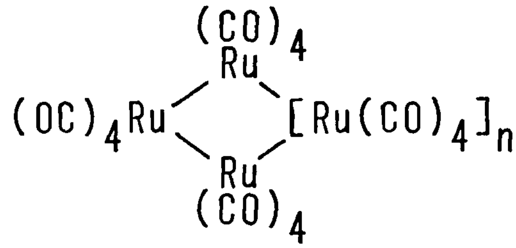
Compound **IV** is extremely insoluble in most solvents with which it does not react and, in spite of numerous attempts, we have been unable to grow crystals suitable for a single crystal X-ray crystallographic study. Powder diffraction studies show, however, that the compound is crystalline. For the same reasons, attempts to obtain molecular weight measurements have proven fruitless as well. The compound is also extremely non-volatile, and we have been unable to obtain useful mass spectral data. FAB-MS studies (suspensions in sulpholane, glycerol) were rather inconclusive, although peaks at m/e values possibly corresponding to $Ru(CO)_4^+$, $Ru_2(CO)_n^+$ (n= 1-8),

$Ru_2C(CO)_n^+$ (n= 1-7) and Ru_n^+ (n= 1-5) were observed.

Compound IV is thus a tetracarbonyl compound of ruthenium, related to III chemically and, quite likely, structurally. As shown above, there are striking similarities between the reactions of IV and III with carbon monoxide, hydrogen, bromine, iodine and carbon tetrachloride. We have carried out for purposes of comparison all of the relevant reactions of III, as reported in the literature, finding close correspondence with the chemistry of IV. In all cases, reaction mixtures and isolated products were characterized utilizing a Bruker IFS 85 FTIR spectrometer equipped with an Aspect 2000 computer. Precision in measuring carbonyl stretching frequencies was very high, and compositions of mixtures were readily established by comparisons with literature data and, in some cases, by spectral subtractions. Thus the nature and relative amounts of the products could be established with certainty.

The suggestion that IV is an isomer of III is supported by the observation that the solid state IR spectra of III and IV are very similar (Fig. 1). Although of relatively low resolution because of broadening inherent in the sampling of solids, the ranges of frequencies of the carbonyl stretching and bending modes of the two compounds are quite comparable, suggesting a similarity in the electron density on the ruthenium atoms in the two compounds. While the molecularity of IV is as yet unknown, its low solubility and volatility suggest polymeric or oligomeric structures, either linear (A) or cyclic (B). Interestingly, attempts to sublime IV resulted only in decomposition at about 126° C to give a black material exhibiting no ν(CO) in its IR spectrum; no volatile, ruthenium-containing material was obtained.

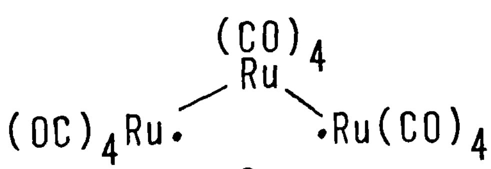




A B

The existence of "open" clusters of either type, not based on geometrical structure of high symmetry, appears not to have been reported previously[16]. However, such structures would appear to explain the lack of formation of cluster compounds in the reactions with tertiary phosphines, as occurs with III[15]. Quite possibly crystals of IV consist of a mixture of homologues of differing molecular weight; this hypothesis would explain the greater apparent broadening in the IR spectrum of IV. While far from definitive, the FAB-MS data are also consistent with the hypothesis of a polymeric or oligomeric structure.

As $Ru(CO)_5$ (I), once formed, decomposes to form $Ru_3(CO)_{12}$ (III) rather than IV, it seems likely that IV forms as a primary product during the photolysis of III, a process which has received attention from several groups. Thus Wrighton et al[17] have proposed the occurrence of homolytic fission to give the diradical C during the photocatalysed isomerization of 1-pentene by III.



C

It was suggested that C was formed by excitation of an electron from a metal-metal bonding orbital into a metal-metal antibonding orbital.

However, two other groups[5,18,19] have found that the photogenerated species seems rather inert towards carbon tetrachloride, behaviour unexpected of a diradical such as A, and have proposed carbonyl-bridged intermediates as alternatives. While we have little to offer in this continuing controversy[20], we note that there appears to be a correlation between the relative amounts of I and IV which are formed and the initial concentration of III. Thus IV is only obtained when the concentration of III is high, consistent with an oligomerization process. On this basis coupling of diradicals C would appear to be a reasonable route to a polymer or a cyclic oligomer containing repeating [$Ru_3(CO)_{12}$] units.

As mentioned above, a compound appearing to be IV has been previously prepared in THF but not characterized[4]. We had initially assumed that the material reported and subsequently obtained by us was a THF adduct and hence of little interest. It was only when we obtained it in hydrocarbon solvents as well that we suspected a new binary carbonyl compound. A similar material also appears to have been prepared by James et al[21], who obtained an insoluble purple solid formulated as $[HRu(CO)_3]_n$ from the carbonylation of aqueous solutions of ruthenium trichloride. We have repeated the synthesis of this material, and find that it has an IR spectrum and an X-ray powder diffraction pattern similar (but not identical) to the corresponding data for IV. We find that the purple solid reacts with iodine to form cis-$Ru(CO)_4I_2$ quantitatively and, as the original evidence for the hydride ligand was indirect, we suggest that the material obtained from aqueous solution is an isomer of IV.

Acknowledgements

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10. We note a possibly unresolved controversy concerning the structure and IR spectrum of this compound[8,9]. The structure (7) illustrated on p. 673 of ref. 1 appears also to be incorrect.

11. No attempt was made to separate the products, but the spectral data leave little doubt about their identity. For similar compounds, see Bennett, M. A.; Bruce, M. I.; Matheson, T. W. in "Comprehensive Organometallic Chemistry"; Wilkinson, G.; Stone, F. G. A.; Abel. E. W., Eds; Pergamon Press: Oxford, 1982, Chap. 32.2, and references therein.

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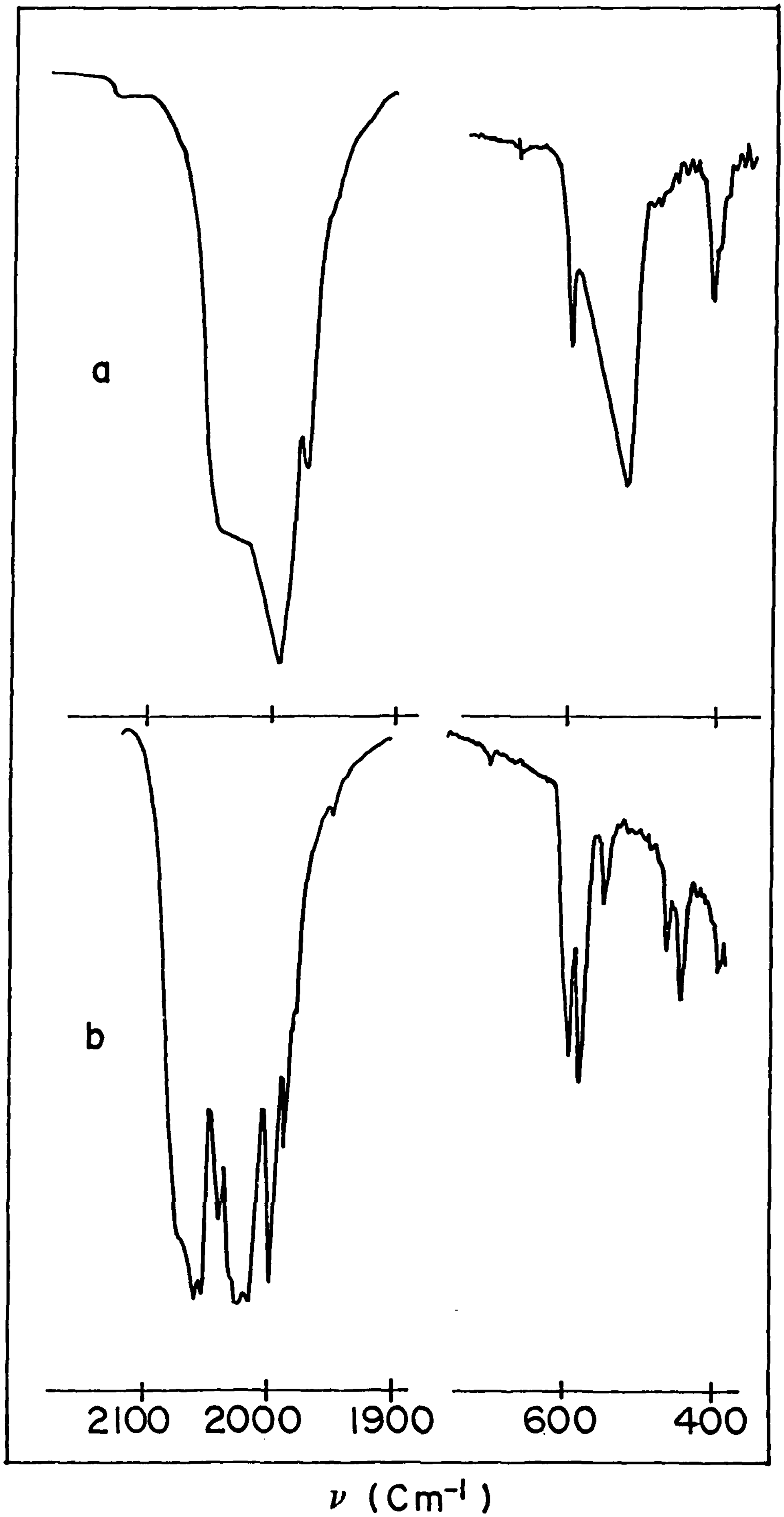
Caption for Figure 1:

Figure 1. IR spectra (KBr discs) of $[Ru(CO)_4]_n$ (a) and $Ru_3(CO)_{12}$ (b).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